

Study on quenching effect of nitrite ions on zinc oxide modified by polyvinylpyrrolidone

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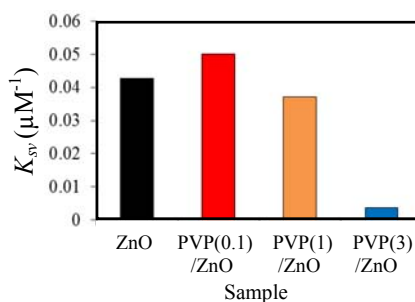
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GRAPHICAL ABSTRACT



ABSTRACT

Zinc oxide (ZnO) is appeared to be an attractive material for application for multidisciplinary fields, owing to its unique physical and chemical properties. In this study, ZnO was synthesized using the co-precipitation method, where the zinc acetate was used as the precursor. The ZnO was further modified by adding different amounts of polyvinylpyrrolidone (PVP) via simple physical mixing method to obtain PVP/ZnO composites. The ZnO and the PVP/ZnO composites were characterized using Fourier transform infrared (FTIR), diffuse reflectance ultraviolet-visible (DR UV-Vis), and fluorescence spectroscopy. The FTIR spectra detected the presence of ZnO group and the functional groups from the PVP. The PVP peaks become more apparent with the increase of the PVP amount. From the DR UV-Vis spectra, no significant change was observed after modification with the PVP, and all composites showed similar broad absorption band to that of the ZnO. The fluorescence spectra showed that the addition of PVP decreased the emission intensity and red shifted the peak wavelength, indicating certain interactions between the ZnO and the added PVP. Quenching study was investigated in the presence of nitrite ions (NO_2^-) with various concentrations (2-10 μM). A linear Stern-Volmer plot was observed and the highest quenching constant rate (K_{sv}) was obtained on the PVP/ZnO sample with PVP content of 0.1 wt%. This study demonstrated that the addition of the PVP on the ZnO improved the interaction between the ZnO and the NO_2^- , which will be one of the important factors for sensing and catalytic applications for detection and conversion of NO_2^- .

Keywords: zinc oxide, polyvinylpyrrolidone, quenching study, fluorescence, nitrite ion

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1. INTRODUCTION

Zinc oxide is one of the key technological materials with great properties and potential applications in numerous fields. Since ZnO is a wide band gap semiconductor with band gap energy of 3.37 eV at room temperature, it has been used significantly for catalytic, electrical, optoelectronic, and photochemical applications [1]. ZnO also has high ultraviolet (UV) absorption, large volume to area ratio specifically for the ZnO nanoparticles, and long life decay which this unique characteristic makes ZnO a versatile catalyst [2,3]. As a semiconductor photocatalyst, ZnO covers a high band gap at about 3.37 eV and absorbs light up to 400 nm [4]. The ZnO has been also reported acting as a good sensor for various environmental remediation and monitoring [5,6].

For most applications in catalysis, photocatalysis and sensing technologies, one of the important factors to be developed is improving the capability of the ZnO to interact with the target molecules. In this study, nitrite ion (NO_2^-) is employed as the target molecules. NO_2^- is a toxic

and hazardous compound, which exists in food as a preservative and environment as a result of excessive use of fertilizer in agricultural land. In agricultural area, when human ingest the fertilizer polluted water, the ingested nitrite can be converted to carcinogenic nitrosamine in human digestive system [7]. In order to increase the interactions between the ZnO and the NO_2^- , the ZnO needs to be further modified.

One of the potential modifiers is polymer and polymeric materials. It is known that the surface modification of ZnO by grafting certain polymers is an effective way to enhance not only the dispersability in polymer matrix, but also the properties of the resulting composites [8]. In recent years, various polymer and polymeric materials have been used to modify ZnO, such as polyethylene oxide [9], poly[2-methoxy-5-(20-ethyl hexyloxy)-phenylenevinylene] [10], carbon nitride [11], and poly(methylmethacrylate) (PMMA) [12]. In this study, the ZnO was modified with polyvinylpyrrolidone (PVP) since the PVP has good fluorescence property and has been

reported to give good interactions with nitrate ions (NO_3^-) [13].

2. EXPERIMENTS

2.1 Material Preparations

To prepare ZnO, zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, QRĕc) was used as a precursor. Solution A was prepared by dissolving 6.4 g of sodium hydroxide, (NaOH , QRĕc) and 7.28 g of cetyltrimethylammonium bromide (CTAB, Fisher Scientific) in 100 mL of unionized water, followed by stirring for 1 h to obtain the homogeneous solution. Meanwhile, solution B was prepared by dissolving 4.5 g of the $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in 100 mL of deionized water and subjected to sonication for 30 min. The solution B was then slowly added to the solution A and heated at 70 °C for 1 h. The obtained remaining solid was filtered and the obtained solid was washed with deionized water and ethanol (EtOH, HmbG), successively. The obtained solid powder was left to dry at room temperature and then calcined at 500 °C with a heating rate of 1.0 °C/min for 1 h to obtain the ZnO [14].

On the other hand, the PVP/ZnO composites were prepared by mixing certain mass of polyvinylpyrrolidone K60 (PVP, Sigma Aldrich) with the prepared ZnO, to produce series of PVP/ZnO composites with various mass ratios of PVP to ZnO. The composites were denoted as PVP(x)/ZnO, where $x = 0.1, 1, 3$ wt%. For the synthesis of PVP(1)/ZnO, 1 g of the ZnO was physically mixed with 0.01 g PVP solid which later ground to obtain the fine mixture of the PVP(1)/ZnO composite. The similar procedure was carried out for other PVP/ZnO composites.

2.2. Characterizations

The properties of the ZnO and the PVP/ZnO samples were investigated using several instruments. The Fourier transformation infrared spectroscopy (FTIR, Thermo Scientific, Nicolet iS50) was used to detect the presence of various functional groups that exist in the samples. Diffuse reflectance UV-Vis spectroscopy (DR UV-Vis, Shimadzu, UV2600) was used to investigate the optical property of the samples. The fluorescence spectroscopy (JASCO, FP-8500) was used at room temperature to examine the fluorescence properties of the samples. The emission spectra of the samples (0.3 g) were monitored at excitation wavelength of 365 nm.

2.3 Quenching Test

The interactions between the samples and the NO_2^- were studied using a fluorescence spectroscopy (JASCO, FP-8500) at room temperature. The quenching tests were carried out, where the samples were exposed to various concentrations of NO_2^- (2-10 μM , 10 μL) and the emission spectra were measured at 365 nm. The interactions between

the samples and the NO_2^- were evaluated from the Stern-Volmer plots using the Stern-Volmer equation, where the relative emission intensity in the absence and presence of the NO_2^- was plotted towards the concentration of the NO_2^- .

3. RESULTS AND DISCUSSION

The chemical structure of the synthesized ZnO and the PVP/ZnO samples were examined using FTIR spectroscopy. Figure 1 shows the FTIR spectra for the ZnO, the PVP/ZnO samples, and the PVP as the reference. As shown in Figure 1 (a), the prepared ZnO showed a sharp peak at 419.97 cm^{-1} that was responsible for the stretching mode for Zn-O [15], indicating the successful synthesis of the ZnO. All the PVP/ZnO samples showed the presence of Zn-O stretching as well as two peaks appeared at 1525 and 1423 cm^{-1} that were assigned to C=O and C-N stretching, which came from the PVP. As shown in the Fig. 1(e), the PVP showed two main peaks at 1650.50 and 1423.52 cm^{-1} that were assigned to C=O and C-N stretching [16]. The shifting observed on the PVP/ZnO samples might be due to the hydrogen bonding and electrostatic interaction between the ZnO and the functional group in the PVP [15]. When the amount of PVP in the PVP/ZnO composite increased, the intensity of C=O stretching and C-N stretching also increased due to the increment amount of PVP containing in PVP/ZnO composites. The peak observed around 3000 cm^{-1} was assigned to CH stretching while around 700 cm^{-1} was assigned to C-C stretching vibration. The peak observed at 3446.83 cm^{-1} was assigned to the OH stretching vibration. The OH peak might come from water molecules that were present in the composites. This happened because the PVP is hydrophilic in nature, which causing the composites to adsorb moisture from the atmosphere.

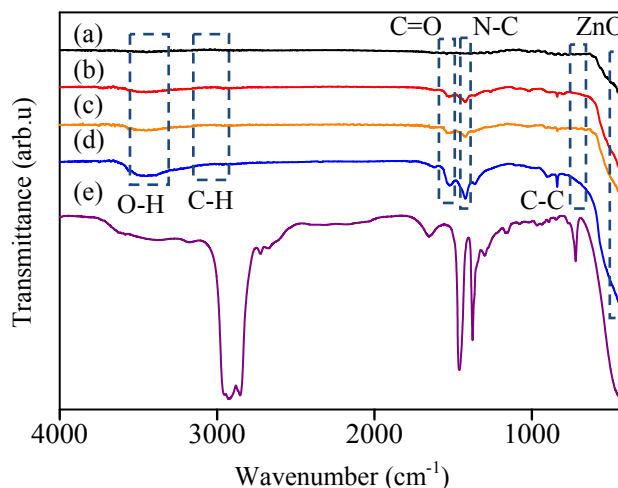


Fig. 1 FTIR spectra for (a) ZnO, (b) PVP(0.1)/ZnO, (c) PVP(1)/ZnO, (d) PVP(3)/ZnO, and (e) PVP

The optical property of the ZnO, the PVP/ZnO samples, and the PVP was investigated using DR UV-Vis

spectroscopy. From Fig. 2(a), the ZnO that gave a strong and broad peak centered at 330 nm, suggesting its capability to absorb UV light region and high transparency in the visible range [17]. While all PVP/ZnO samples showed the absorption peak of ZnO, increasing the loading amount of the PVP slightly increased the absorption band around 370 nm. As shown in Fig. 2(e), the PVP showed intense narrow bands centered at 265 and 370 nm, indicating the presence of C=O and N-C groups, respectively. The band centered at 265 nm may be assigned to $n \rightarrow \pi^*$ transition between the oxygen lone pairs and the vacant π^* orbital of the pyrrolidone ring. The absorption band appeared at 370 nm might be due to the charge-transfer transitions of electrons excited from the carbonyl lone pair to the adjacent carbon atom in pyrrolidone ring [18].

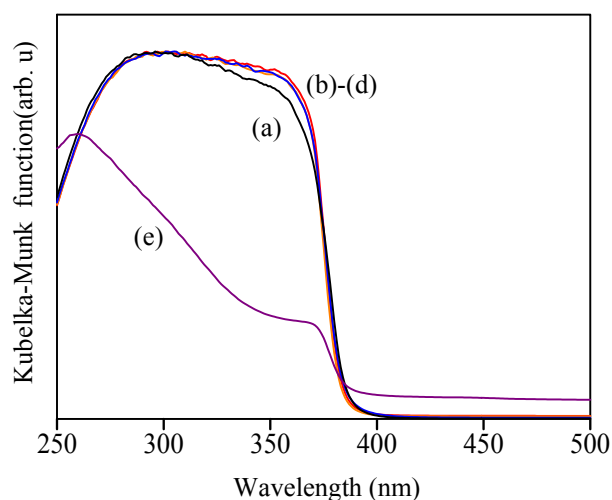


Fig. 2 DR UV-Vis spectra for (a) ZnO, (b) PVP(0.1)/ZnO, (c) PVP(1)/ZnO, (d) PVP(3)/ZnO, and (e) PVP

Figure 3 shows the emission spectra of the prepared ZnO and PVP/ZnO composites. As shown in Fig. 3(a), ZnO showed the emission peak at 517 nm when excited at 365 nm. The emission peak at 517 nm has been recognized as the green emission of ZnO, reflecting the presence of oxygen defect on the surface and deep level of the ZnO [19]. On the other hand, all the PVP/ZnO composites have lower emission intensity compared to the ZnO. The fluorescence intensity of PVP/ZnO composites decreased because of the surface defect level increased the nonradiative transitions [20]. Other than the reduced emission intensity, the addition of PVP shifted the emission peak to longer wavelength. The decrease in fluorescence intensity and the peak shifting strongly indicated that there were interactions exist between the PVP and ZnO [21]. The results of the fluorescence spectra were found to be in good agreement with the results of the FTIR spectra.

The as-prepared ZnO and the composite were further tested for its ability to interact with the hazardous NO_2^- . The interaction ability of ZnO and the composites towards the NO_2^- was investigated using Stern-Volmer

plot, where the obtained gradient represented the interaction strength. In the Stern-Volmer plot, the relative emission intensity can be expressed as a function of the NO_2^- concentrations, according to the Stern-Volmer equation (Eq. 1),

$$\frac{I_o}{I} = K_{sv}[Q] + 1 \quad (1),$$

where I_o and I are emission intensities obtained in the absence and presence of NO_2^- , respectively, Q is the concentration of NO_2^- , and K_{sv} is the Stern-Volmer quenching constant. Figure 4 shows the emission spectra for ZnO, where the increase in concentration of NO_2^- (0-10 μM) further quenched the emission intensity. The Stern-Volmer plot is shown in the inset of Fig. 4, where the relative emission intensity was found to be in a linear function with the increase in the NO_2^- concentration (0-10 μM). This result clearly indicated that there is interaction between the ZnO sample and the NO_2^- . One of the possible interactions would be an electrostatic interaction [22]. The K_{sv} value for the ZnO was determined to be $0.04 \mu\text{M}^{-1}$.

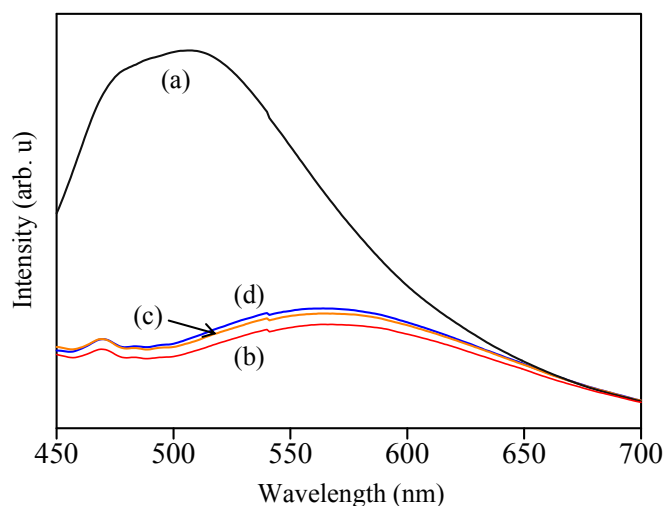


Fig. 3 Emission spectra for (a) ZnO, (b) PVP(0.1)/ZnO, (c) PVP(1)/ZnO, and (d) PVP(3)/ZnO

Similar linear Stern-Volmer plots were also obtained on the PVP/ZnO samples (not shown). These results suggested that the PVP/ZnO samples were also able to interact with the NO_2^- . The comparison on the K_{sv} values between the ZnO and the PVP/ZnO is shown in Fig. 5. It was clear that the addition of PVP gave improvement on the K_{sv} value of the ZnO when the loading of the PVP was low, *i.e.*, 0.1 wt%. The K_{sv} value increased from 0.04 to $0.05 \mu\text{M}^{-1}$. This 25% improvement showed the contribution of the PVP to increase the interaction to the NO_2^- . Unfortunately, when the loading of PVP increased to 1 or 3 wt%, the K_{sv} value of the ZnO decreased since the high loading of PVP may block the emission sites of the ZnO. Less emission sites of the ZnO would result in the less sensitivity. This study showed that only small loading of

PVP can help to improve the interaction between the ZnO and the NO_2^- .

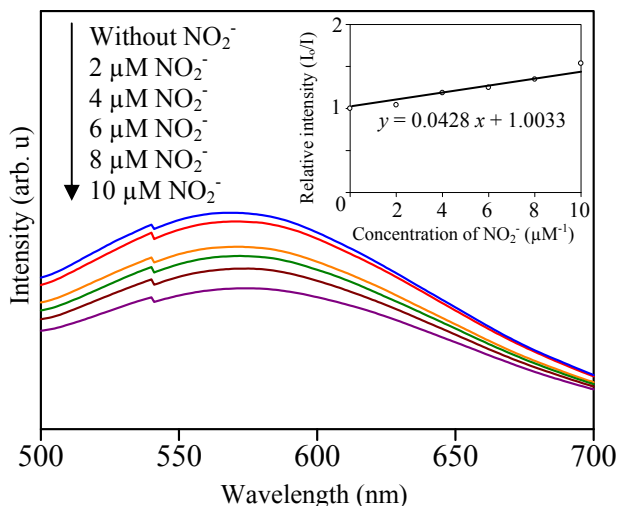


Fig. 4 Quenching of the emission intensity for the ZnO with the presence of NO_2^- (2-10 μM). The inset shows the Stern-Volmer plot for the ZnO

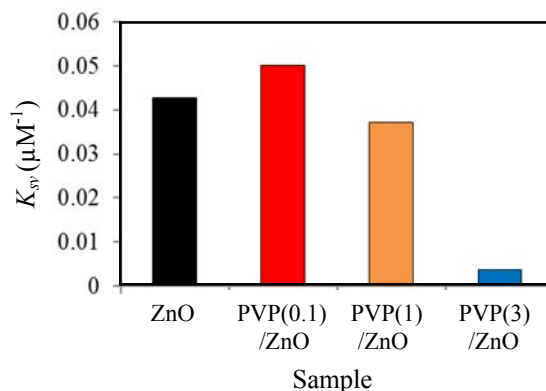


Fig. 5 K_{SV} values of the ZnO and the PVP/ZnO composites

4. CONCLUSION

The ZnO and PVP/ZnO composites were successfully synthesized via co-precipitation and simple physical mixing methods, respectively. The FTIR and DR UV-Vis spectra showed that the addition of the PVP did not change the chemical properties of ZnO. The fluorescence spectra showed that addition of the PVP reduced the emission intensity and caused shifting of the emission peak. From the quenching study, the linear Stern-Volmer plots for ZnO and PVP/ZnO in the presence of NO_2^- with various concentrations suggested the good interaction between the ZnO and the PVP/ZnO composites towards the NO_2^- . Only modification with small amount of the PVP (0.1 wt%) can give a 25% improvement on the K_{SV} value of the ZnO.

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